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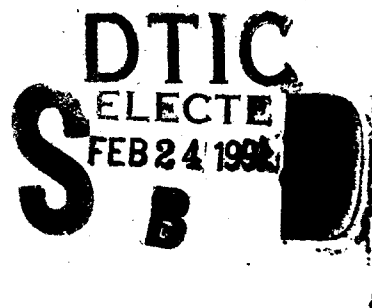
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PROGRESS ON POLYMER DEGRADATION BY PHOTOELECTRON TRANSFER

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13. ABSTRACT (Maximum 200 words) 1,5-Bis(3-hydroxypropoxy)-9,10-dimethoxyanthracene has been prepared and incorporated into poly (2-butyne diyl oxalate). The photolysis results of the copolymer are described. Progress toward the preparation of 2-(4-carboxyphthalimoyl)-9,10- dimethoxyanthracene from 2-amino-9,10-anthraquinone and mellitic anhydride is described. Synthetic intermediates have been characterized by ultraviolet/visible, infrared and proton nuclear magnetic resonance spectroscopy.				
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PREFACE

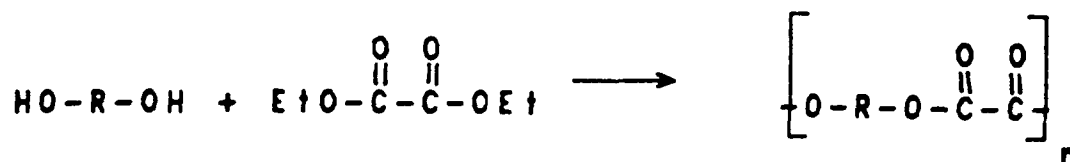
The work described in this report was authorized under Program Element Number 1L161102, Project Number AH5202050, an Work Unit Number A00 entitled Advanced Materials and covers the period from May 1990 to August 1991. The report discusses the synthesis of anthracene compounds that may be effective photoelectron transfer reagents and catalysts for polymer degradation.

PROGRESS ON POLYMER DEGRADATION BY
PHOTOELECTRON TRANSFER

INTRODUCTION

For some time this laboratory has been interested in energy absorptive materials, specifically polymers which could decompose cleanly to gaseous products on thermal or photic excitation. We recently reported the synthesis of some unsaturated polyoxalates according to the following equation and their characterization.¹ The thermal decomposition of these polymers was studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and mass spectroscopy.

The polyoxalates of cis-2-butene-1,4-diol (1), trans-2-butene-1,4-diol (2) and 2-butyne-1,4-diol (3) were synthesized. For comparison to these unsaturated polyoxalates, the polyoxalate of 1,4-butanediol (4) was also prepared. Polymers were prepared by transesterification of equimolar mixtures of the diol and diethyl oxalate.



The polymers were characterized by ¹H-NMR spectra run in DMSO-d₆. Since the chemical shifts of the end groups were sufficiently different from those of the internal groups, it was possible to determine molecular weights and degree of polymerization (DP) values by NMR end group analysis. The DP values reported were in the range 7-32. The molecular weights of polymer samples were subsequently determined by vapor phase osmometry in acetonitrile using a UIC070 Basic Osmometer. The osmometric molecular weights were in good agreement with those obtained by NMR.

The unsaturated polyoxalates proved to be more thermally stable than originally anticipated. Evidence was presented for the thermal degradation of 1-P and 2-P to 1,3-butadiene and CO₂ and of 3-P to butatriene and CO₂. It was shown that initiation of this thermal degradation was by homolytic O-CH₂ bond scission (rather than OC-CO bond cleavage). This fact leads to a rapid "unzipping" of the polymer chain by successive loss of CO₂ and diene or triene.

RESULTS AND DISCUSSION

Studies of the photochemical decomposition of these unsaturated polymers have shown that solutions 1-P and 3-P in acetonitrile-d₃ undergo slow decomposition upon irradiation in the presence of 9,10-dimethoxyanthracene (DMA).² Photoexcited DMA is known to be a good single electron donor. The mechanism of photodegradation of the unsaturated oxalates is believed to proceed by electron transfer from DMA to an oxalate unit in the polymer. The transient oxalate radical anion would then degrade by successive loss of CO₂ and 1,3-butadiene or butatriene.

It was decided to test this mechanism by studying the photolysis of an unsaturated polyoxalate that had a DMA unit incorporated into the polymer chain. Therefore 1,5-bis(3-hydroxypropoxy)-9,10-dimethoxyanthracene (BHPDMA) 5 was synthesized from 1,5-dihydroxy-9,10-anthraquinone by modification of published procedures: alkylation with 3-chloro-1-propanol³ was followed by reductive methylation of the anthraquinone⁴ using phase transfer catalysis, yielding the desired product. (See Figure 1.)

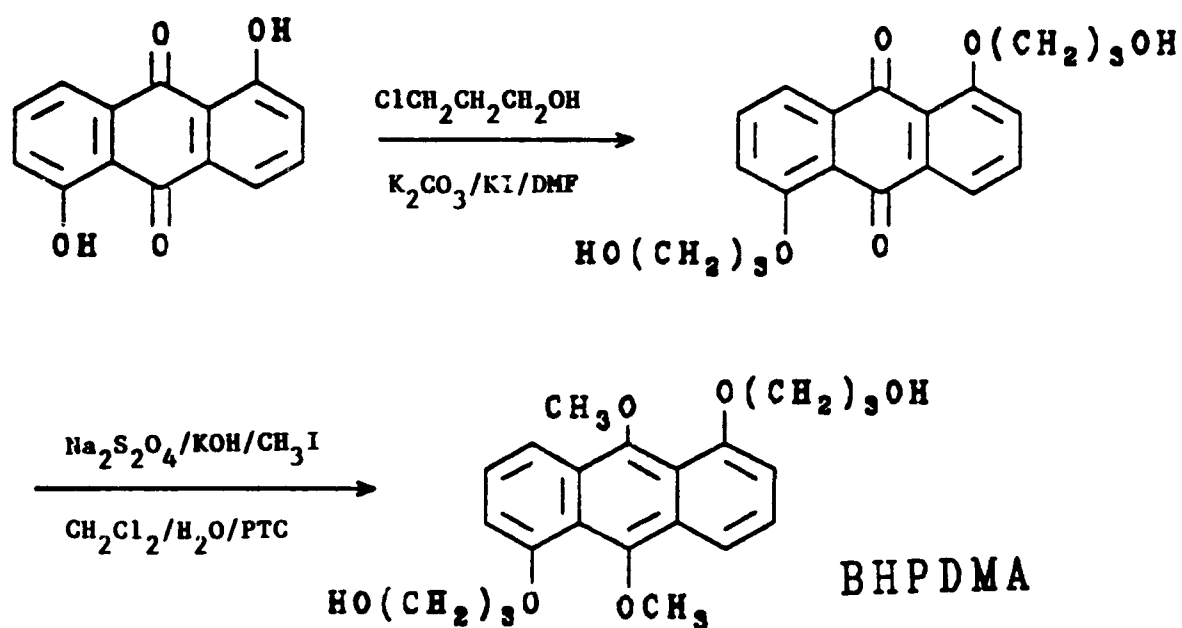


Figure 1. BHPDMA was characterized by infrared, ^1H NMR, UV and mass spectrometry.

BHPDMA was incorporated into poly(2-butyne-1,4-diyl) oxalate 3-P by heating a 1:18 molar ratio of the two compounds at 115°C under vacuum. The product copolymer 3,5-P was a yellow solid that was purified by addition of methanol to an acetone solution of the polymer. Since MeOH is a nonsolvent for the polymer, this procedure leads to precipitation of higher molecular weight material. There is good evidence for the incorporation of BHPDMA units into 3-P. Their UV spectra (EtOH) have absorption maxima at 358, 375, 392 and 415 nm, almost identical to the absorption pattern of BHPDMA itself and characteristic of dimethoxyanthracenes.

The IR spectrum (KBr) of copolymer 3,5-P is similar to that of 3P with the following notable exceptions: appearance of an aromatic C-H stretch at 3010 cm^{-1} and appearance of aromatic C=C stretches at 1620 and 1535 cm^{-1} that are characteristic of BHPDMA. The 250 MHz ^1H NMR spectrum (CD_3CN) of the copolymer indicates the incorporation of a small number of BHPDMA units into the polymer. Absorptions at 7.92 ppm (d), 7.48 ppm (dd) and 6.87 ppm (d) are assigned respectively to $\text{H}_{2,6}$; $\text{H}_{3,7}$ and $\text{H}_{4,8}$ of the anthracene ring. The internal CH_2 groups of the butyne-1,4-diyl units absorb at 4.95 ppm (s). Comparison of the NMR integration indicates approximately 5% incorporation of BHPDMA, i.e., about 20 butyne-1,4-diyl units for each BHPDMA. Molecular weight determination by vapor phase osmometry in CH_3CN gave a value of 899 g/mole for the copolymer. This result would give a DP value of 6-7 for the copolymer. It is assumed that BHPDMA insertion into polymer 3-P is random, although this assumption has not been examined yet.

NMR and IR spectroscopy indicate that the end groups of the copolymer 3,5-P are OH groups. A sample was treated with bis (trimethylsilylacetamide) in CH_3CN to convert the terminal OH groups to trimethylsiloxy groups. This trimethylsilylated copolymer was then irradiated in a Rayonet photoreactor at 350 nm in CD_3CN . The NMR spectrum indicated little polymer decomposition after 16 hours irradiation; even the 3-P/DMA mixture showed substantial decomposition after four hours. It was thought that electron transfer might be slow for steric reasons and that under the conditions of low photon flux, the major process may be photooxidation of the dimethoxyanthracene unit.

Attention was then turned to the preparation of a more flexible dimethoxyanthracene unit. It was thought that having a good electron acceptor near the dimethoxyanthracene might facilitate photoelectron transfer and accelerate polymer decomposition. A synthesis of 2-(4-carboxyphthalimidoyl)-9,10-dimethoxyanthracene 6 was sought. The commercially available starting materials for the synthesis were 2-amino-9,10-anthraquinone and trimellitic anhydride (1,2,4-benzene-tricarboxylic anhydride). The synthetic scheme is shown in Figure 2. A similar scheme starting with 1-amino-9,10-anthraquinone to produce 1-(4-carboxyphthalimido)-9,10-dimethoxyanthracene has also been explored, but to this point most of the effort has been on the 2-substituted anthraquinones since they have greater steric flexibility.

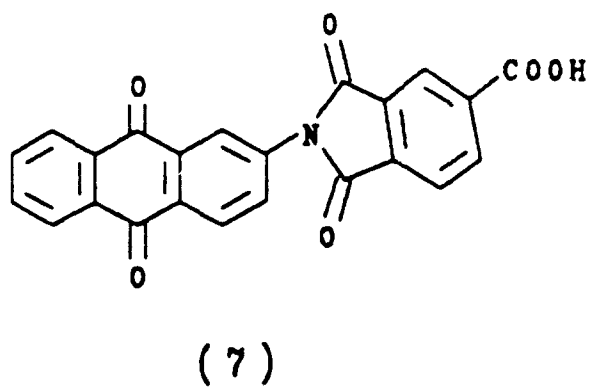
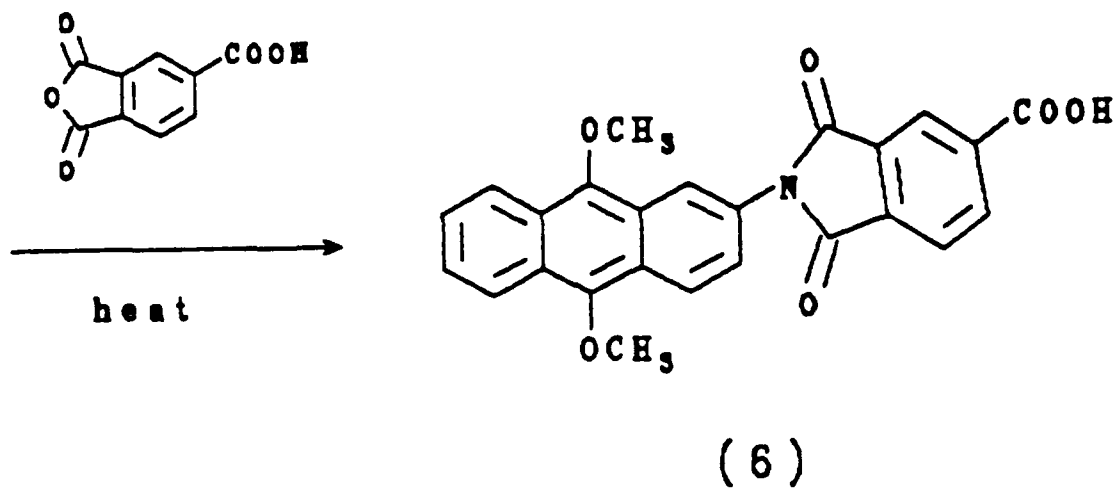
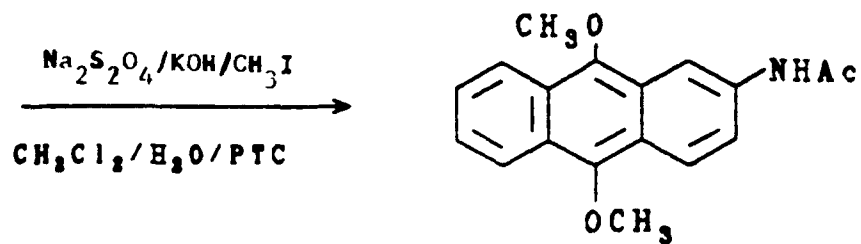
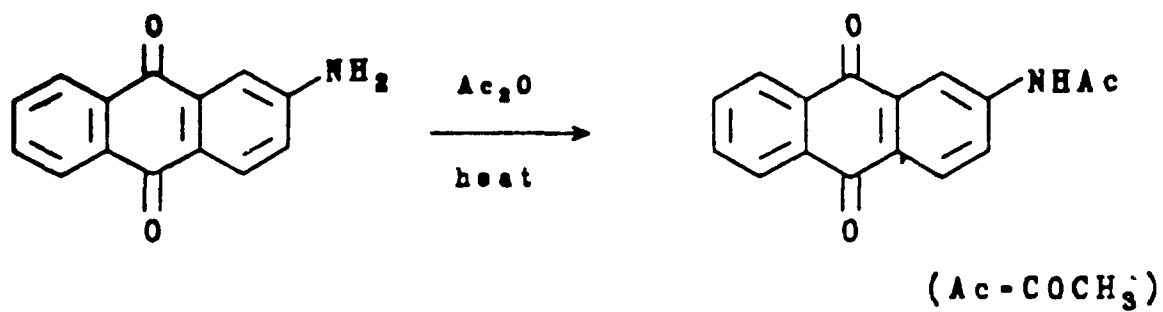


Figure 2. The Synthetic Scheme.

Both 1- and 2-amino-9,10-anthraquinone are converted to their acetamido derivatives in about 90% yield by heating with acetic anhydride. The amides were characterized by infrared (KBr), UV/vis (MeOH), and ^1H NMR (DMSO- d_6) spectroscopy. Spectral data were all in accord with the proposed structures.

Attempts were made to prepare 2-(4-carboxyphthalimido)-9,10-anthraquinone (7) by heating either 2-amino-9,10-anthraquinone or 2-acetamido-9,10-anthraquinone with mellitic anhydride under a variety of conditions. We have evidence for the formation of 7 (most notably the appearance of peaks at 1780 and 1730 cm^{-1} in the infrared characteristic of 5-membered ring imides⁵), but the compound decomposes in methanol solution. It is believed that the phthalimide group of 7 is particularly labile to nucleophilic attack because of the presence of the electron-withdrawing carbonyl groups of the anthraquinone unit and the carboxyl.

At this point efforts were directed toward doing the reductive methylation first and then introducing the imide functionality as indicated in Figure 2. The methoxy substituted imide 6 would be expected to be more stable than 7 toward nucleophilic attack.

Reductive methylation of 2-acetamido-9,10-anthraquinone with sodium dithionite, potassium hydroxide and methyl iodide in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ using trioctylmethylammonium chloride as a phase transfer catalyst gave 2-acetamido-9,10-dimethoxyanthraquinone. In order to get good conversion to product, it was necessary to use long reaction times and to replenish the reagents periodically. The gold-colored crystals of the product

melted at 245-247°C. Both the IR spectrum (KBr) and ^1H NMR spectrum (DMSO- d_6) are consistent with the assigned structure. Tentative NMR assignments are given in Table 1.

Table 1. NMR Assignments

<u>Proton(s)</u>	<u>Integration</u>	<u>ppm</u>	<u>Multiplicity</u>
N-H	1H	10.27	s
H ₁	1H	8.62	s
H _{4,5,8}	3H	8.19	m
H _{3,6,7}	3H	7.4-7.7	m
OCH ₃	6H	4.02, 4.00	s,s
COCH ₃	3H	2.13	s

SUMMARY, CONCLUSIONS & RECOMMENDATIONS

The preparation of a series of unsaturated polyoxalates has been reported previously. They degrade thermally to give CO₂ and 1,3-butadiene or butatriene. It has also been shown that they degrade photochemically in the presence of 9,10-dimethoxyanthracene, a good electron donor.

In the present work, incorporation of a 9,10-dimethoxyanthracene unit into poly(2-butyne-diyl) oxalate 3-P is reported. One attempt at photodegradation of the copolymer was unsuccessful, perhaps for steric reasons. It is recommended that efforts to photolyze this copolymer

continue. Among experiments that could be undertaken are the use of higher photon fluxes, using laser photolysis to focus the light at a wavelength of maximum absorption of the DMA unit, and the preparation of copolymers with larger amounts of BHPDMA and higher molecular weights.

Substantial progress toward the synthesis of 2-(4-carboxyphthalimido)-9,10-dimethoxyanthracene (6) has been made. A preliminary experiment indicates that 6 can be formed efficiently by heating 2-acetamido-9,10-dimethoxyanthracene and mellitic anhydride. It is recommended that efforts toward the synthesis of 6 and its incorporation into a polymer chain be continued.

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